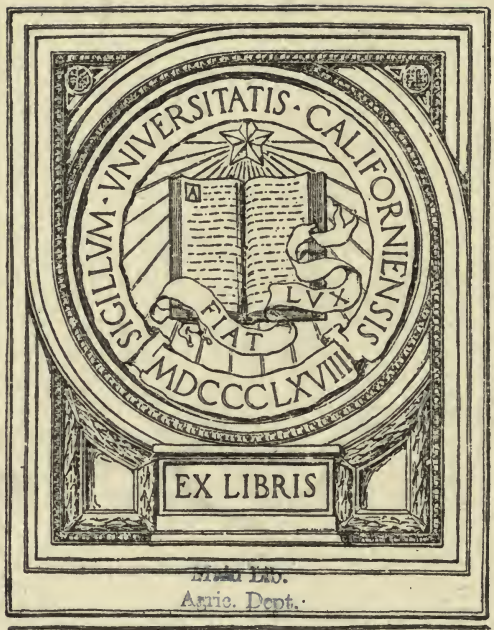
UC-NRLF
B 3 088 403


SIGILLVM · VNIVERSITATIS · CALIFORNIENSIS
LVX
FIAT
MDCCCLXVIII
EX LIBRIS

Agric. Dept.

Digitized by the Internet Archive
in 2007 with funding from
Microsoft Corporation

http://www.archive.org/details/chemicalmethodsf00veitrich

Issued August 29, 1907.

U. S. DEPARTMENT OF AGRICULTURE,

BUREAU OF CHEMISTRY—CIRCULAR NO. 36.

H. W. WILEY, CHIEF OF BUREAU.

CHEMICAL METHODS FOR UTILIZING WOOD,

INCLUDING DESTRUCTIVE DISTILLATION, RECOVERY OF TURPENTINE, ROSIN, AND PULP, AND THE PREPARATION OF ALCOHOLS AND OXALIC ACID.

By

F. P. VEITCH,

Chief, Leather and Paper Laboratory.

4208—No. 36—07——1

WASHINGTON : GOVERNMENT PRINTING OFFICE : 1907

LIBRARY OF THE UNIVERSITY OF CALIFORNIA

LETTER OF TRANSMITTAL.

U. S. Department of Agriculture,
Bureau of Chemistry,
Washington, D. C., May 10, 1907.

Sir: The demand for information as to the nature and uses of the chemical compounds manufactured from wood and the processes and equipment used in their production has become so general that it is not possible to supply the desired data through the channels of correspondence. To meet this need, the accompanying manuscript has been prepared, and I recommend its publication as Circular 36 of the Bureau of Chemistry. The requests received are largely with reference to the disposal of waste materials, and although the questions involved are rather technical no effort has been made to produce an elaborate treatise on this subject, but rather to explain the processes as simply as the subject-matter will permit.

The utilization of wood wastes in chemical manufactures is attracting much attention at the present time, and the information here given is especially of interest in view of the temporarily depressing effect which the use of denatured alcohol will have on the demand for wood alcohol.

While investigations made in this Bureau furnish much of the data given, acknowledgments are due to Hon. C. F. Wright, Mr. C. J. Root, Mr. Joseph Bennor, and Mr. J. J. Mallonee for general information, and to Messrs. Struthers-Wells & Co., Klar's Technologie der Holzverkohlung and Sjöstedt in the Iron Age for January 28, 1904, for illustrations of apparatus.

Respectfully,

H. W. Wiley.
Chief Bureau of Chemistry.

Hon. James Wilson,
Secretary of Agriculture.

CONTENTS.

	Page.
Introduction	7
Statistics of wood distillation	7
Properties of wood affecting yield of products	9
Specific gravity and weight	9
Water content	10
Composition	10
Yield of distillation products from different woods	11
Apparatus for destructive distillation	12
Description of equipment	12
Cost of plant	15
Manufacturing processes	17
General process of distillation	17
Nature of the reactions in the retort	20
Special features of the distillation of pine, fir, and spruce	22
Crude products of destructive distillation	23
1. Noncondensable gases	24
2. Charcoal	24
3. Tar and oils	24
Wood tar	24
Wood oil	27
Additional oils obtained from resinous woods	28
Wood turpentine	29
Pine oils	30
Rosin spirits	31
Rosin oils	31
Tar oils	31
4. Aqueous distillate of crude pyroligneous acid	32
General treatment for the separation of acetic acid and methyl alcohol	32
Acetic acid	33
Aluminum acetate	35
Chromium acetate	35
Copper acetate	35
Lead acetate	35
Sodium acetate	35
Crude methyl alcohol and acetone	35
Pure methyl alcohol	37
Acetone	37
Recovery of certain wood products by treatment with chemicals	39
Treatment with soda, soda ash, or volatile solvents	39
Preparation of ethyl alcohol from sawdust	40
Production of acetic acid and acetates by fusion with alkalies	40
Manufacture of oxalic acid	41
Suggestions for the development of these industries	43
Yields	44
Operating expenses	44
Raw materials	46

ILLUSTRATIONS.

		Page.
FIG. 1.	Early form of kiln in which only charcoal is recovered	12
2.	Early form of kiln in which charcoal and tar are recovered	12
3.	Early kiln for recovery of alcohol and acid	13
4.	Swedish thermo-kettle	13
5.	Round retort with condenser	14
6.	A modern oven retort	14
7.	Types of condensers	15
8.	Wood car used in oven retort	17
9.	Charcoal cooler used with oven retort	18
10.	Plan of a modern American destructive distillation plant	18
11.	Plan of a refining apparatus	19
12.	Plan of German type of fractional distillation plant	20
13.	Retorts used in distilling turpentine	22
14.	Diagram showing the processes and products of the destructive distillation of wood	26
15.	Liming still	33
16.	Still for preparing acetic acid from acetate of lime, with detail of acetate pan	34

DESTRUCTIVE DISTILLATION PRODUCTS OF WOOD, INCLUDING THEIR NATURE AND USES AND OTHER CHEMICAL METHODS OF MANUFACTURE.

INTRODUCTION.

Each year there are millions of cords of wood wasted in the forest and on the farm. This wood, because of its shape, size, or quality, is not suitable for the numerous mechanical uses for which wood is employed, and information regarding other means of disposing of this waste is of general interest. Aside from tanning and paper making, which are chemical industries that have been established for hundreds of years, there are other industrial uses, of more recent origin, which are of agricultural importance because they offer a means of utilizing these wastes of the sawmill and the forest. The more important of these are destructive distillation, recovery of turpentine, rosin, and paper pulp, preparation of alcohols, and manufacture of acids. The growth of some of these industries has been rapid in recent years, and is not due alone to the demand for a method of utilizing the waste woods of lumbering operations, such as tops, sawdust, slabs, and timber too small to be profitably handled for lumber, but also to a steadily increasing demand for wood alcohol, acetates, acetone, turpentine, charcoal, etc., in other industries. In the past the demand for these products has been sufficient to encourage the steady growth of the industries engaged in their production, and the values of the products have been well maintained, except in so far as the passage of the law permitting the tax-free use of denatured alcohol has affected the price of wood alcohol.

STATISTICS OF WOOD DISTILLATION.

Of the various processes employed for manufacturing chemical compounds from wood, that of destructive distillation is probably at present the most important. The industry is an old one, and is quite well developed in Germany, Russia, Norway, and Sweden, and less extensively in France and England.

The following table gives some idea of the more important data pertaining to this industry as compiled by the United States Census and the Forest Service of this Department:

Amounts and values of wood-distillation products in the United States.

Year.	Number of establishments.	Products.					
		Crude alcohol.		Acetate.		Charcoal.	
		Amount.	Value.	Amount.	Value.	Amount.	Value.
		Gallons.	*Dollars.*	*Pounds.*	*Dollars.*	*Bushels.*	*Dollars.*
1880	17	.....	86,274	6,593,000	156,892	.....	.....
1890	53	1,116,075	688,764	26,778,415	315,430	.....	.....
1900 [a]	93	4,945,963	1,976,986	86,828,000	981,286	17,154,302	726,672
1904 [b]	118	6,684,870	2,161,813	105,141,361	1,474,982	23,869,055	1,197,973
1905 [c]	[d] 67	5,062,076	.....	86,685,129	.....	[e] 26,670,139	.....
1906 [f]	(d)	5,273,103	.....	103,337,630	.....	45,656,720	.....

[a] Capital invested, $5,499,876; cords of wood used, 490,939.
[b] Capital invested, $10,506,979; cords of wood used, 586,114, value, $1,783,004; lime used, 523,334 bushels, value, $101,068; soda used, 371,780, value, $5,484.
[c] Cords of wood used, 659,770, value, $2,010,611.
[d] Hardwood distillation alone. According to statistics collected by the Census Bureau and the Forest Service, the average value of hardwood varies from $1.84 to $3.51 per cord.
[e] Tar and oil, 677,480 gallons.
[f] Cords of wood used, 1,144,896.

The distribution of the factories in 1900 is shown in the following table:

Distribution of factories and number of hands employed, 1900.

State.	Number of plants established.	Wage-earners employed.
Pennsylvania	58	578
New York	24	354
Michigan	5	169
North Carolina	3	12
New Jersey, Indiana, Massachusetts	3	74

In the Southern States the distillation of waste pine woods is receiving a great deal of attention, but has not yet been placed upon a satisfactory business basis. The statistics of this industry for 1905 as given by the Forest Service and for 1906 by the Census Bureau are as follows:

	1905.	1906.
Establishments	15	.....
Cords of wood used	16,969	50,234
Value of wood per cord	$1.74 to $3.00	.....
Total value of raw material	$42,805	.....
Products:		
Charcoal.....bushels..	300,106	791,887
Tar.....gallons..	362,500	648,120
Oil.....do....	434,780	125,008
Turpentine.....do....	238,180	503,427

The quantity and value of acetate of lime (gray) and of wood alcohol exported in recent years are given in the statistical abstracts of the Department of Commerce and Labor as follows:

Acetate of lime and wood alcohol exported 1898–1906.

Year.	Wood alcohol.		Acetate of lime.	
	Quantity.	Value.	Quantity.	Value.
	Proof gallons.	*Dollars.*	*Pounds.*	*Dollars.*
1898	385,938	199,230	37,496,288	537,856
1899	727,062	414,875	48,987,511	700,000
1900	540,799	320,306	47,790,765	776,413
1901	919,504	476,582	61,296,544	1,101,037
1902	626,925	338,619	60,296,544	962,265
1903	833,629	452,892	59,449,811	987,067
1904	1,194,466	585,359	64,256,945	1,103,389
1905	1,097,451	603,385	55,170,131	1,245,776
1906	780,222	466,467	69,363,624	1,950,833

From these figures it appears that the export trade in wood alcohol and acetate of lime, while it fluctuates from year to year, shows a notable increase during the past nine years.

PROPERTIES OF WOOD AFFECTING YIELD OF PRODUCTS.

Methyl alcohol, acetates, acetone, charcoal, turpentine, wood oil, and oxalic acid are directly or indirectly obtained on a commercial scale from woods, and the yield is governed largely by the specific gravity, weight per cord, and kind of wood, as well as by the manner in which the manufacturing process is conducted. Many other farm products, such as sugar cane, cornstalks, straws, cotton stalks, etc., will yield these products, and it is possible that many other wastes may in the future be utilized in this way. So far, however, but little attention has been given to these materials, and for economic reasons they are not commercially employed.

SPECIFIC GRAVITY AND WEIGHT.

Different kinds of wood have different specific gravities, and even samples of the same species differ in this respect. Specific gravity figures are, therefore, of general value only, and can not be considered as strictly applicable to any particular lot of wood. The weight of a cord of wood varies not only with the specific gravity of the wood but also with the way in which it is piled, a closely piled cord weighing, of course, more than a loosely piled one. It has been found that as a rule there is 44 per cent of vacant space in a cord of wood as usually put up, but 56 per cent of the 128 cubic feet being actually wood. These facts undoubtedly account in part for the widely different yields so frequently reported and must be considered carefully in making calculations of yield of products in which wood is usually expressed in cords and not by weight. The specific gravity, weight per cubic foot, and ash of certain American woods, as deter-

mined by Sharpless, are quoted from the Report of the Tenth United States Census. The figures given are the average for different varieties of the same species.

Specific gravity and weight of different woods.

Kind of wood.	Specific gravity.	Ash.	Weight per cubic foot.	Weight per cord.
		Per cent.	*Pounds.*	*Pounds.*
Ash	0.6251 to 0.7184	0.26 to 0.78	38.9 to 46.8	2,790 to 3,350
Oak	.6540 to .9501	.26 to 1.49	40.7 to 59.2	2,920 to 4,220
Chestnut	.4504	.18	28.0	2,010
Beech	.6883	.51	42.9	3,070
Birch	.5760 to .6553	.25 to .31	35.9 to 40.8	2,570 to 2,920
Poplar	.3889	.96	24.2	1,740
Elm	.6506	.80	40.5	2,910
Longleaf pine	.6999	.25	43.6	3,120
Norway pine	.4854	.27	30.2	2,160
White pine	.3854	.19	24.0	1,720
Spruce	.4051 to .4584	.27 to .32	25.2 to 28.6	1,810 to 2,050
Hemlock	.4239	.46	26.4	1,890
Douglas fir	.5157	.08	32.1	2,300
Larch	.6236	.33	38.8	2,780
Maple	.5269 to .6912	.33 to .54	32.8 to 43.1	2,300 to 3,090

WATER CONTENT.

The wood used for destructive distillation should be as dry as possible, as much time and fuel are wasted if green or wet wood must be dried in the retort and the temperature raised under such conditions to the point at which distillation begins. For these reasons it is the best practice to cut and stack the green wood, which contains from 20 to 50 per cent of water, from eight months to two years before it is to be used in order that it may become well seasoned. Even seasoned woods contain from 12 to 25 per cent of water, which must be evaporated in the retort before the disintegration of the wood begins.

The capital required to maintain a two years' supply of wood for a plant using 20 cords of wood a day varies from $20,000 to $40,000, so that in many instances wood not thoroughly seasoned is used in preference to making this outlay. Such a practice, of course, increases the operating expenses considerably, and drying ovens heated by the waste steam and gases of the plant have been used in some cases to dry the wood quickly before it goes into the retort. This is undoubtedly the better practice, and whenever it is possible plants should be equipped with such drying ovens, thus decreasing the amount of capital invested in wood and at the same time securing large yields, as during seasoning by exposure wood loses weight from rotting and from the solution of water-soluble constituents, and consequently gives a lower yield of distillation products.

COMPOSITION.

The data on the composition of wood are not very satisfactory, as most of the figures were obtained by methods less accurate than those now in use. Neither were as many normal constituents of woods

determined as can now be estimated. In the following table of analyses, made by Hugo Müller, the figures for water extract are probably much too low, and include a number of definite and known substances, such as tannins, coloring matter, sugars, starch, etc., while a number of other definite compounds which it is now possible to estimate are covered by the term "incrusting matter."

Analyses of various woods (Müller).

Kind of wood.	Water.	Water extract.	Resins.	Cellulose.	Incrusting matter.
	Per cent.	*Per cent.*	*Per cent.*	*Per cent.*	*Per cent.*
Birch	12.48	2.65	1.14	55.52	28.21
Beech	12.57	2.41	.41	45.47	39.14
Oak	13.12	12.20	.91	39.47	34.30
Alder	10.70	2.48	.87	54.62	31.33
Lime	10.10	3.56	2.93	53.09	29.32
Chestnut	12.03	5.41	1.10	52.64	28.82
Fir	12.87	4.05	1.63	53.27	28.18
Poplar	12.10	2.88	1.37	62.77	20.88
Pine	13.87	1.26	.97	56.99	26.91
Willow	11.66	2.65	1.23	55.72	28.74

It may be said further with reference to these figures that at present no definite relation can be established between the composition of woods and the chief distillation products obtained from them, namely, alcohol, acetic acid, acetone, and charcoal. The data available, however, indicate that cellulose gives maximum yields of methyl alcohol and but little acetic acid when subjected to destructive distillation, the latter product being evidently derived chiefly from the more unstable "incrusting matter."

YIELD OF DISTILLATION PRODUCTS FROM DIFFERENT WOODS.

While any kind of wood may be used for the production of alcohol, acetates, and charcoal, the hard woods give much larger yields than do the soft woods, while resinous woods yield the most turpentine, wood oils, and tar. Of the hard woods the maple, birch, beech, and oak are preferred, although other woods, such as poplar, elm, willow, aspen, and particularly alder, give nearly as high yields. The quantities of the several products obtained in modern plants from one cord of wood are shown in the following table:

Amount of products yielded per cord of wood.

Classes of woods.	Charcoal.	Alcohol (crude) containing acetone.	Acetate of lime.	Tar.	Wood oils.	Turpentine.	Gas.
	Bushels.	*Gallons.*	*Pounds.*	*Gallons.*	*Gallons.*	*Gallons.*	
Hard woods	40 to 50	8 to 12	150 to 200	8 to 20	.....	.....	.....
Resinous woods	25 to 40	2 to 4	50 to 100	30 to 60	30 to 60	[a] 12 to 25 [b] 2 to 10	.....
Sawdust (hardwood)	25 to 35	2 to 4	45 to 75	.....	.....	.....	.....

[a] Lightwood. [b] Sawdust.

The wide variations in quantity obtained from the same class of materials are due to differences in quality and weight of the wood used and also to different methods of conducting the distillation. The low yield obtained from sawdust is rather surprising, and is probably explained by the packing of the material in the retorts, owing to which fact complete decomposition is rarely obtained. As far as can be learned no satisfactory process has yet been devised for distilling sawdust.

APPARATUS FOR DESTRUCTIVE DISTILLATION.

DESCRIPTION OF EQUIPMENT.

The apparatus required for the destructive distillation of wood consists of (1) retorts or ovens, in which the distillation is carried on and

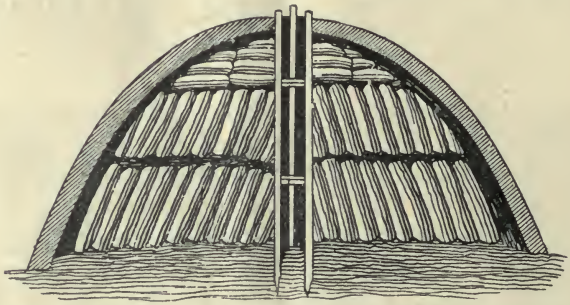


FIG. 1.—Early form of kiln in which only charcoal is recovered.

the chief chemical reactions involved in the production of the crude products take place; (2) condensers, in which the condensable vapors are liquefied; (3) stills, in which the crude products are separated,

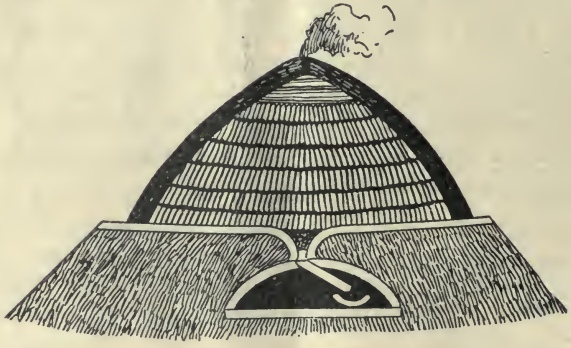


FIG. 2.—Early form of kiln in which charcoal and tar are recovered.

concentrated, and purified; (4) mixing pans for the preparation of acetate of lime, and (5) general apparatus, such as evaporating pans, storage tanks, coolers, pumps, etc.

The various forms of kilns in which wood was formerly charred are of historic interest, especially in connection with the modern improved retorts; but as the yield of alcohol and acetate is very low even in the best kilns, these old forms are now employed only in localities producing charcoal iron, where charcoal is practically the only product recovered. Figures 1, 2, and 3 illustrate these early forms of kilns. The yield of condensed products in a kiln, such as is shown in fig. 3, is about one-half that from a modern retort.

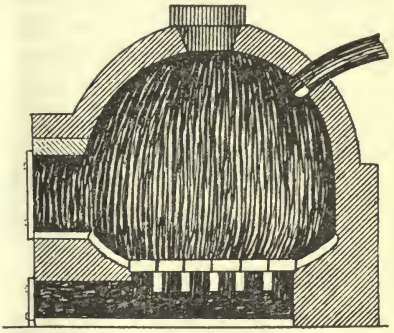


FIG. 3.—Early kiln for recovery of alcohol and acid.

When attempts were made to recover and condense the volatile products an air-tight iron retort (fig. 4), known as the "Swedish thermo-kettle," set in brickwork and connected with a condenser, was devised and is still quite extensively employed abroad, where it has been in use since 1857. The round retort (fig. 5), which is a modified and later form of the above, is made of three-eighths inch steel, is 9 feet long and 50 inches in diameter, and is provided with a large, tightly fitting door at one end and an outlet pipe, about 15 inches in

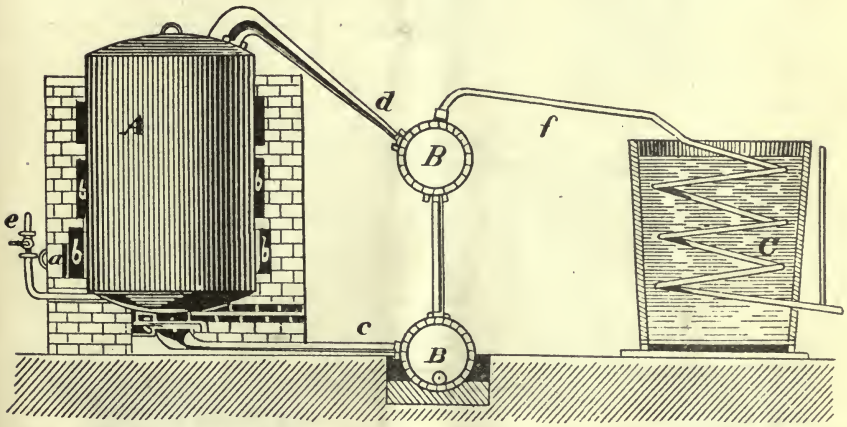


FIG. 4.—Swedish thermo-kettle: *A*, retort; *a*, furnace; *b*, spiral flue; *c*, tar pipe; *d*, neck conducting the gases; *B*, drums where tar vapors condense and collect; *C*, condenser; *e*, steam pipe; *f*, pipe conducting acid vapors to condenser.

diameter, connected with the condenser at the other end. The retorts are preferably set horizontally in pairs in brickwork, and batteries of from 6 to 16 pairs are common. The chief objection to this form of retort is that, as usually built, it must be filled and emptied by hand,

thus making the cost of operating high. To obviate this objection, what is known as the oven retort (fig. 6) was devised and in recent

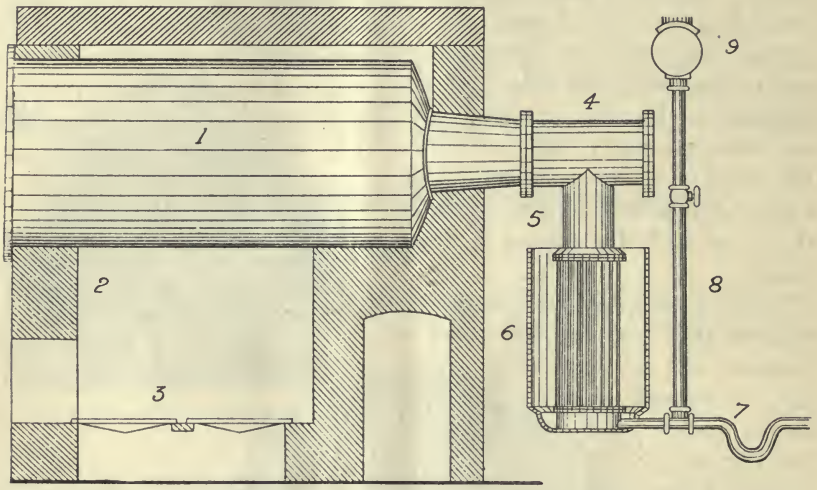


FIG. 5.—Round retort with condenser: *1*, retort; *2*, fire walls; *3*, grate; *4*, neck; *5*, pipe to condenser; *6*, condenser; *7*, trapped delivery pipe; *8*, gas pipe; *9*, gas main.

years has been largely used in equipping new plants for hardwood distillation. These retorts are rectangular iron chambers, a common size being 6 feet wide, 7 feet high, and from 27 to 50 feet long, accord-

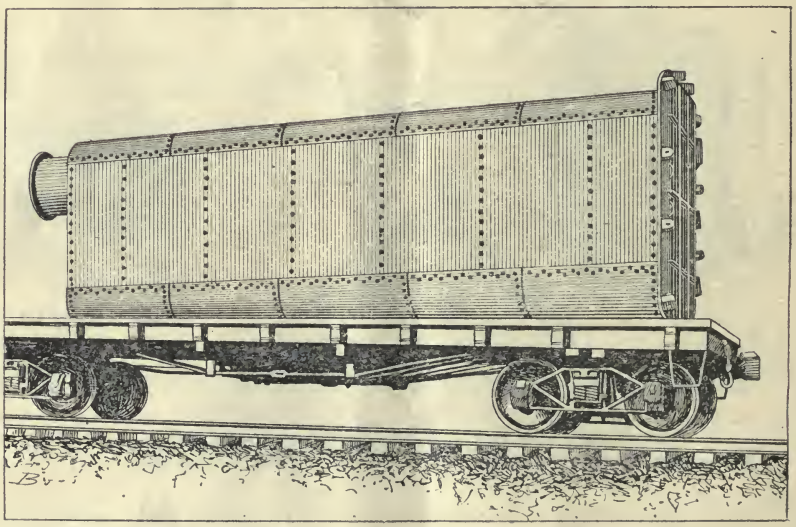


FIG. 6.—A modern oven retort.

ing as they are intended to hold two or more cars loaded with wood. The ovens are set in brickwork, or are made with double iron walls

with an air space between. They are provided with large doors closing air tight and are heated by wood, charcoal, coal, or gas.

The plant may be assembled and arranged in any desired manner, but it is highly desirable that full advantage be taken of natural conditions, that as much labor as possible be performed by machinery, and that the whole establishment be conducted under the most rigid control, in order that the plant may be profitably worked and losses at any point quickly discovered. Modern plants are equipped with either the round or oven retorts. Figures 10, 11, and 12 show arrangements of such plants as found in American and German practice.

The condensers (fig. 7) are of the greatest importance; they should be sufficiently large to condense all the products even under the most adverse conditions, as material lost at this stage can never be recovered. For separating the constituents of the distillate a simple still,

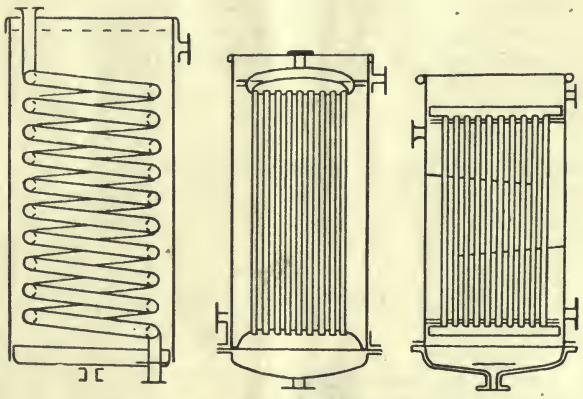


FIG. 7.—Types of condensers.

such as is used in the preparation of distilled liquors, may be used, although an iron still is generally preferred in distilling the alcohol and acetone from the acetate of lime. For tar storage and settling tanks it is customary to use wood; all pipes, pumps, and other apparatus through which the acid liquors pass must be of copper or wood.

COST OF PLANT.

Only approximate figures can be given as to cost and quantity of equipment for the destructive distillation of wood, as any figures would be greatly modified by the location of the plant, local price of labor, freight charges, royalties on patents, and completeness of equipment. The first cost of equipment may often be greatly reduced by cheap construction and by omitting many labor and time saving devices in

apparatus, but such a procedure increases running expenses and is the most costly in the end.

Builders of destructive-distillation plants quote from $1,500 to $2,000 per day-cord on a basis of a 10-cord plant, with higher figures for smaller plants and lower figures for larger ones.

The price of equipment when turpentine alone is recovered by distilling with steam is, as a rule, considerably lower than the destructive equipment, and quotations vary from $400 to $1,500[a] per cord of wood treated daily. These wide differences are due largely to the newness of the industry in the South, to differences in time of distillation, and also to the fact that in nearly all cases the apparatus is patented and an exorbitant value is frequently placed on the patent rights.

A plant to destructively distil 12 cords of wood per day will require, approximately, the following equipment:

2 oven retorts, each 32 feet long, or 12 round retorts.
4 oven coolers, each 32 feet long, or 100 100-pound charcoal cans.
24 to 26 charcoal cars of iron (if oven retorts are used).
1 tar still.
1 liming still.
1 alcohol still.
1 steam pan, 14 feet long, 9 feet wide, 6 inches deep.
1 settling pan, 8 feet long, 9 feet wide, 4 feet deep.
1 100-horsepower boiler.
1 10-horsepower engine.
1 set iron mixing gear.
1 blow tank for elevating liquid acetate to settling tank.
1 storage tank.
1 mixing tub, wood.
2 to 3 wooden storage tanks.
1 copper condenser for each retort.
1 copper column still and condenser.
Pumps to supply water for condenser.

In the case of pine-wood distillation additional storage and settling tanks for tar and turpentine, another tar still, and a refining still for turpentine are required. Smaller liming and alcohol stills may be used. A plant for the recovery of turpentine only would call for much less equipment, and the apparatus would be of a different character. If a daily charge of 10 cords is to be distilled the following items would probably be sufficient:

10 retorts, capacity of 1 cord each.
10 condensers.
1 150-horsepower boiler.
1 100-horsepower engine.

[a] The higher prices are based on operating each retort but once in twenty-four hours. If the time of distillation is shortened, as can safely be done, the cost per day-cord is reduced proportionally.

1 refining still.
1 condensing coil.
2 hogs for chipping the wood (one in reserve).
Storage tanks for crude and refined turpentine.
Pumps and piping for water supply and turpentine.

These lists of apparatus are merely illustrative, as builders of plants must modify their equipment in accordance with experience and circumstances.

MANUFACTURING PROCESSES.

GENERAL PROCESS OF DISTILLATION.

The round retorts are filled with the wood by hand, two lengths of wood filling a retort, which is made to hold about 1 cord. When

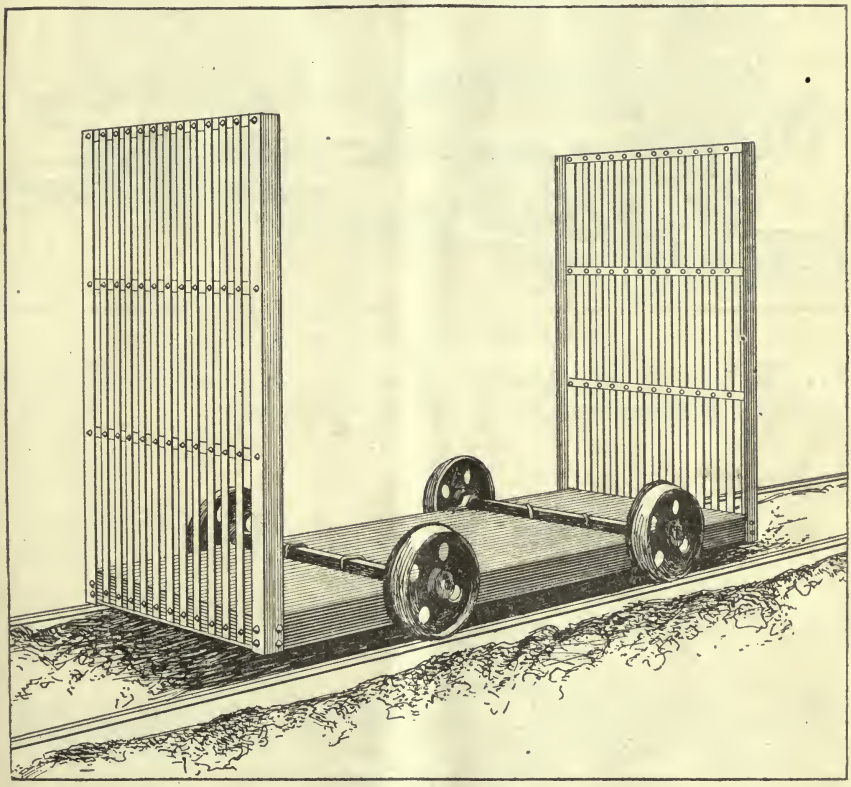


FIG. 8.—Wood car used in oven retort.

ovens are used the wood is loaded on iron cars (fig. 8) holding from 1 to 3 cords of wood, and from 2 to 8 cars are run into the oven. The doors in all cases are made gastight, if possible. The retorts are heated slowly and the distillation is continued for from twenty to thirty hours, the progress being indicated by the flow of liquor and

the gradual heating of the front of the retort from top to bottom. When the entire front of the retort has reached a fairly uniform tem-

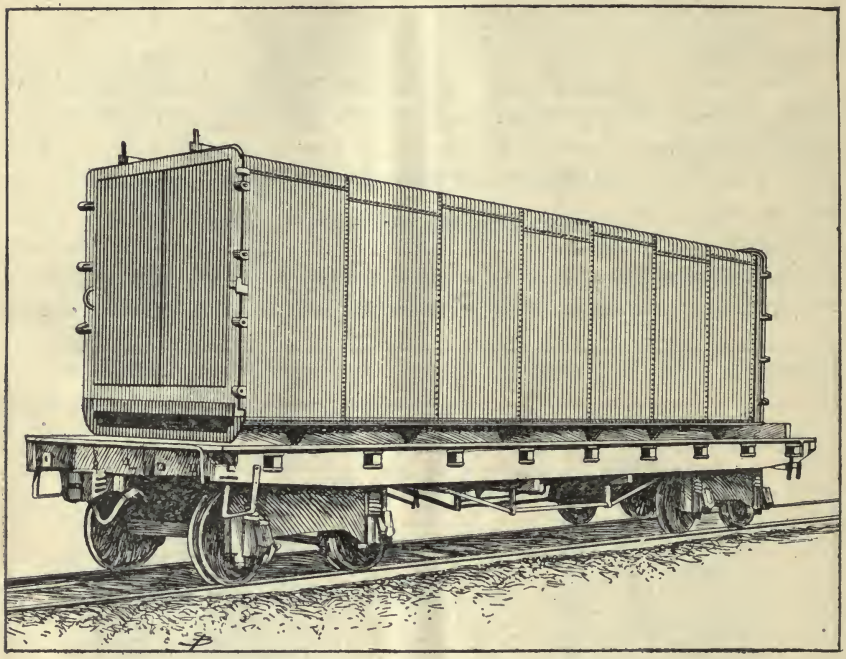


FIG. 9.—Charcoal cooler used with oven retort.

perature the fires are allowed to die down, and, when the retorts or ovens are sufficiently cool, the charcoal is removed.

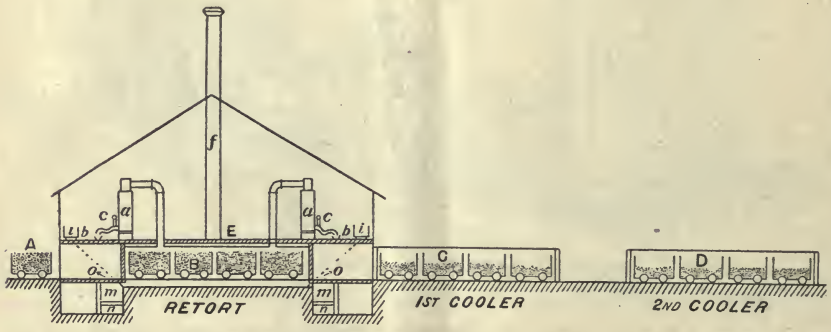


FIG. 10.—Plan of a modern American destructive distillation plant: A, car; B, retort; C, first cooler; D, second cooler; E, acetate drying floor; *a*, condensers; *b*, liquor trough; *c*, gas main to boilers; *i*, fuel conveyor; *m*, fire place; *n*, ash pit; *o*, hinged spout delivering fuel from *i* to *m*.

If retorts are used the charcoal is placed in covered cans, but with ovens, coolers (fig. 9), similar in shape, are used in which the coal

is allowed to remain until thoroughly cool. The time required for distillation, as already stated, varies from twenty to thirty hours and averages about twenty-four hours. The distillate from the retorts passes to the condensers (figs. 5 and 7), where the acid, alcohol, and other valuable constituents are condensed to liquid form and then carried to a large wooden settling tank, which may be either under-

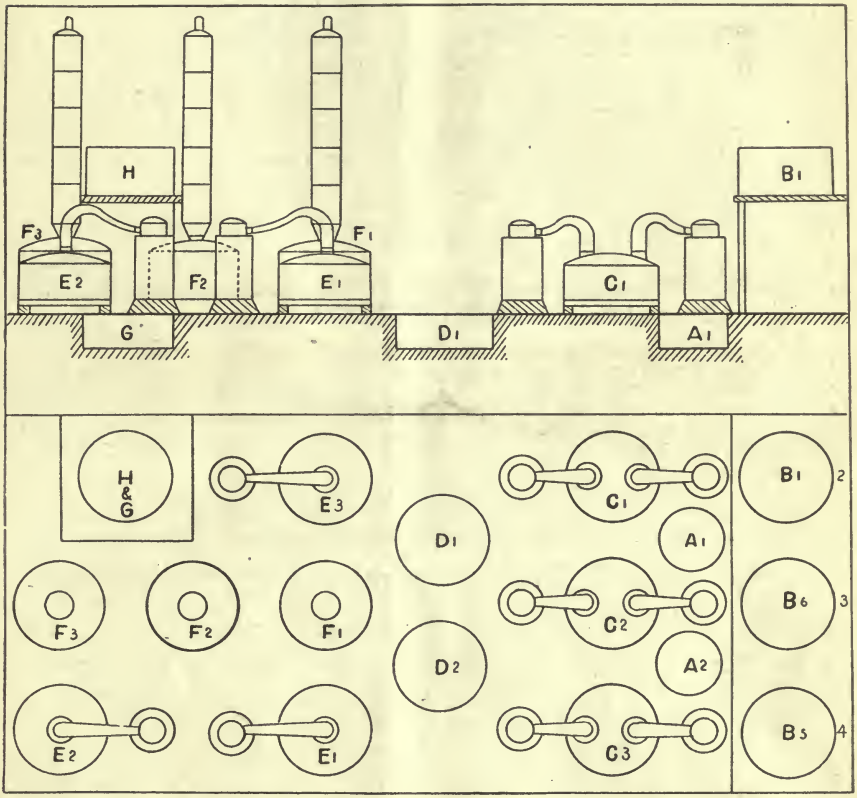


FIG. 11.—Plan of a refining apparatus: A 1-2, raw liquor vats; B 1-6, raw liquor settling tanks; C 1, tar still; C 2-3, raw liquor stills; D 1-2, neutralizing vats; E 1-3, lime-lee stills; F 1-3, alcohol stills; G, weak alcohol storage tank; H, strong alcohol storage tank.

ground or overhead, where it is allowed to stand for several days in order that the tar may settle. The uncondensed gases pass from the condensers to the gas mains (figs. 5 and 10) and are either carried directly to the furnace and burned there or go to a gas holder, from which they are used. If the tar is not otherwise treated it is blown under the boilers with a steam jet and burned. Figures 10, 11, and

12 show the general arrangement of plants. The separation and purification of the products will be described under the several products.

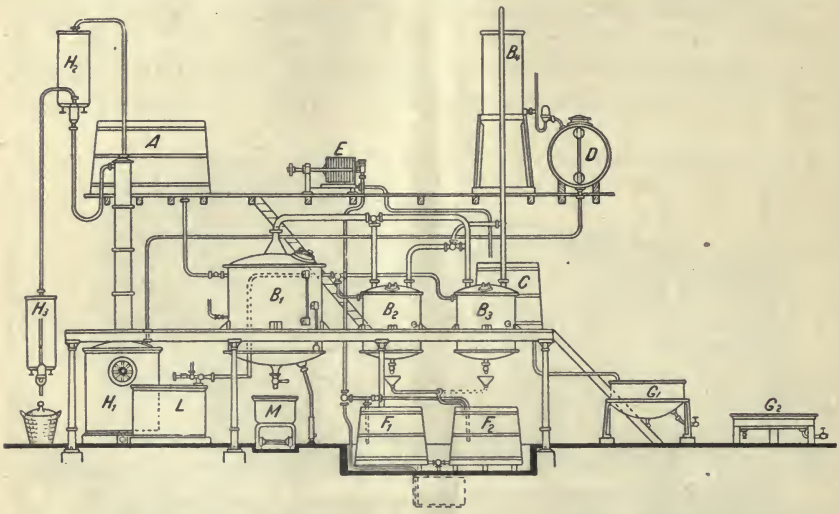


FIG. 12.—Plan of German type of fractional distillation plant: A, reservoir for settling pyroligneous acid; B_1, tar still; B_2, B_3, liming stills; C, vat for filtered acetate liquor; D, reservoir for crude dilute alcohol; E, filter press for acetate liquor; F_1, F_2, F_3, vats for unfiltered acetate liquor; G_1, G_2, evaporating pans for acetate; H_1, H_2, H_3, column rectifying still for concentrating alcohol; L, milk of lime vat; M, boiled tar car.

NATURE OF THE REACTIONS IN THE RETORT.

When hardwood is heated decomposition does not begin until the temperature has reached 150° C., the loss below this temperature being water alone. With resinous woods turpentine begins to distil with water at 97° C. and continues to pass up to about 185° C., overlapping with such products of destructive distillation as may begin to pass over above 150° C. Above this temperature (150°)[a] liquid products resulting from the decomposition of the wood are distilled. The total quantity volatilized, as determined by Violetti, from moisture-free hardwood at different temperatures is shown in the following table:

Percentage of wood volatilized at different temperatures (Violetti).

Temperature.	Amount volatilized.	Residue.	Temperature.	Amount volatilized.	Residue.
° C.	*Per cent.*	*Per cent.*	° C.	*Per cent.*	*Per cent.*
150 to 160	2.00	98.00	260 to 270	62.86	37.14
160 to 170	5.45	94.55	270 to 280	63.84	36.16
170 to 180	11.41	88.59	280 to 290	65.91	34.09
180 to 190	18.01	81.99	290 to 300	66.39	33.61
190 to 200	22.90	77.10	300 to 310	67.13	32.87
200 to 210	26.86	73.14	310 to 320	67.77	32.23
210 to 220	32.50	67.50	320 to 330	68.23	31.77
220 to 230	44.63	55.37	330 to 340	68.47	31.53
230 to 240	49.21	50.79	340 to 350	70.34	29.66
240 to 250	51.33	49.57	350 to 432	81.13	18.87
250 to 260	58.77	40.23	432 to 1,500	82.60	17.31

[a] It is very doubtful whether alcohol, acid, or tar begins to distil before the temperature of the retort reaches 200° C.

THE UNIVERSITY OF CALIFORNIA

From these figures it appears that distillation is, for all practical purposes, complete at 430° C., as the additional volatilization above this temperature is only about 1.5 per cent. The chief products are formed continuously throughout the entire process, which proceeds in three characteristic periods: (1) At a temperature from 150° to 280° C., acetic acid, methyl alcohol, and wood creosote are the chief products; (2) from 280° to 350° C., large volumes of gases are also given off; (3) and from 350° to 430° C., solid hydrocarbons are distilled. Chorley and Ramsay[a] have found that the yields of both methyl alcohol and acetic acid continue up to about 500° C., or at least above 380° C. The quantity of methyl alcohol formed increases with rise of temperature to a maximum at about 300° C. and gradually falls above that temperature, while the quantity of acetic acid formed under the same conditions increases to 350,° with a slight fall in quantity between 350° and 450°. Barillot,[b] on the other hand, found that on a large scale acetic acid ceased to be formed above 300° C. at the end of thirteen hours. On the whole, therefore, it appears that, while the yields of both alcohol and acid have reached the maximum at 300° to 350° C., the formation of both continues up to 450°, beyond which point it is useless to raise the temperature.

Experiments and experience have both shown a lower yield of acid and alcohol when the wood was rapidly heated than when slowly heated, but the experiments of Chorley and Ramsay just cited show that maximum yields of both products may be obtained even when distillation is completed in two or three hours. It appears, therefore, from the data that the low yields obtained from fast heating in practice are due to overheating rather than to rapid heating. In the case of overheating, secondary reactions are set up by the high heat, resulting in the destruction of some of the alcohol and acid. This is particularly liable to occur where no provision has been made to remove the products of distillation from the influence of high heat. Further, when the vapors are evolved rapidly without provision for their prompt removal there is apt to be considerable loss from "blowing of the retorts," that is, the escape of gases around the door due to pressure within the retort. On the other hand, slow distilling allows the vapors to pass out with less loss from blowing or secondary reactions. It is of the greatest importance, therefore, that provisions be made for the rapid removal of the vapors from the retort and for their complete condensation subsequently.

---

[a] J. Soc. Chem. Ind., 1892, **2**: 395.

[b] Compt. rend., 1896, **122**: 735.

SPECIAL FEATURES OF THE DISTILLATION OF PINE, FIR, AND SPRUCE.

As pine, fir, and spruce contain turpentine and rosin, the process of distillation is modified when these woods are used. Figure 13 shows some special forms of retorts for distilling pine. The processes in use are of two general types: Steam distillation and destructive distillation. In the former case live or superheated steam is used to remove the turpentine, which is the only product commercially obtained. During the heating part of the rosin oozes out of the wood but is seldom recovered. When the destructive process is employed the procedure differs from hardwood distillation only in the fact that the temperature in the retorts should be kept below 200° C. until the

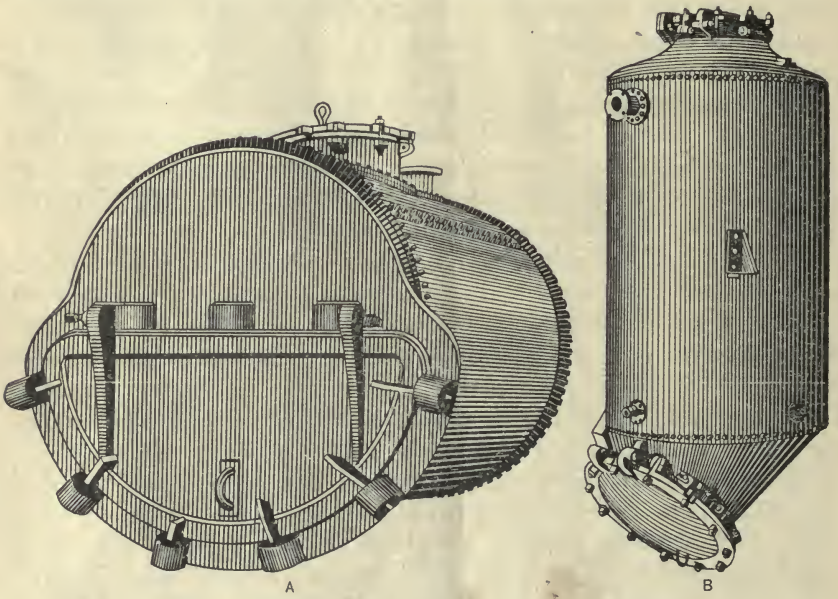


FIG. 13.—Retorts used in distilling turpentine: A, horizontal type; B, vertical type.

turpentine has been driven off, the aim being to keep the turpentine separated from the other products of distillation from which it can not be completely purified if they be allowed to mix. So far this has not been satisfactorily accomplished on an industrial scale owing to the difficulty of preventing local overheating of the retort.

A great number of retorts both for steam and destructive distillation of resinous woods have been invented and patented to meet the special conditions arising in distilling these woods. Many of these have valuable features, while others have no practical advantage over the regular hardwood retorts which have been in use for many years. The yield of turpentine will depend on the richness of the wood, ordi-

nary pine yielding by steam distillation from 2 to 5 gallons per cord, while good light wood yields from 10 to 20 gallons and averages about 15 gallons per cord, and very rich light wood from 20 to 30 gallons. When pine is destructively distilled the yields from good light wood are as follows: Alcohol, from 1½ to 4 gallons; acetate of lime, from 50 to 100 pounds; turpentine, from 15 to 25 gallons; tar, 30 to 60 gallons; charcoal, 25 to 35 bushels; and other wood oils, 30 to 60 gallons. Very few operators recover the acetic acid in any form and so far as is known none of them recover alcohol.

There is one other type of process applicable to the treatment of resinous woods and a few plants have been built to operate on this principle. The wood is treated, in a closed bath connected with a condenser, with a liquid having as high a boiling point as rosin, such as rosin itself, cotton seed oil, etc. Such a process is applicable for the recovery of turpentine and rosin and industrially depends, of course, on the use of a solvent cheap enough to make it a financial success.

With reference to the wood turpentine industry in the South it may be said that, from a careful examination of a large number of plants, the writer is convinced that the distillation industry of the South can not be profitable as a whole until fundamental changes in equipment and in technical and business management are made. In the vast majority of cases the equipment is extremely crude, technical knowledge is lacking, and wasteful labor and business conditions prevail. Both profits and yields of products could be materially increased by improvements in all of these particulars.

CRUDE PRODUCTS OF DESTRUCTIVE DISTILLATION.

The crude products from the distillation divide themselves naturally into four classes, as follows:

	Per cent.
(1) Noncondensable gases	20 to 30
(2) Charcoal	20 to 35
(3) Tar and oils	5 to 20
(4) Aqueous distillate or crude pyroligneous acid	30 to 50

As has been said, it is the American practice to burn the gases and tar under the boilers, particularly in the hardwood districts, but it is highly probable that the tar is too valuable to be thus used and that it could be more profitably disposed of for other purposes.

While the chief and most valuable products of hardwood distillations are charcoal, acetic acid, methyl alcohol, tar, and acetone, a large number of other compounds are produced either primarily or by secondary reactions; and, in the aqueous distillate, formic, propionic,

butyric, crotonic, and valerianic acids; acetaldehyde, furfuraldehyde, methyl-propyl ketone, methyl-ethyl ketone, methyl formate, methyl acetate, etc., have been recognized.

NONCONDENSABLE GASES.

The gases produced during distillation constitute from 20 to 30 per cent of the wood and consist of about 53 per cent of carbon dioxid, 38 per cent of carbon monoxid, 6 per cent of methane, and the remaining 3 per cent of nitrogen, hydrogen, etc. These gases are of such low illuminating power that they are usually either burned under the boilers or retorts or are wasted.

CHARCOAL.

The charcoal left in the retort when distillation is complete constitutes from 20 to 35 per cent of the original weight of the wood, the quantity depending on the kind of wood and the manner of heating the charge. The physical qualities and chemical composition of charcoal are governed chiefly by the temperature at which the wood is heated. When heated to about 280° C., wood begins to be friable and has a brownish black color. At 310° C. it is friable, takes fire readily, and is black in color. The coal becomes harder with further rise of temperature and is less readily ignited. As it is only 25 per cent as heavy as the wood from which it is made charcoal presents some advantages as a fuel, because of lower transportation charges. A good charcoal should be thoroughly burned without being brittle and should show the woody texture distinctly. The fracture should be conchoidal, lustrous, and quite black. It should have few cracks, the specific gravity should be high, and it should burn slowly without flame or smoke.

Charcoal is chiefly used in the manufacture of charcoal iron, for which purpose it is especially valuable, because of its low phosphorus and sulphur content. It is also used to some extent as a domestic fuel and as an absorbent and clarifier.

TAR AND OILS.

Wood Tar.

The crude wood tar produced when wood is distilled in retorts varies from 3 to 10 per cent of the wood. The portion separated from the crude pyroligneous acid by settling and that skimmed off of the top of the neutralized acid are united, and, after washing with water, may be sold in the crude state as "raw tar" or as "retort tar." It is used for preserving wood, for making roofing felts, as an antiseptic,

and for the preparation of wagon grease and other low-grade lubricants. It is also a suitable raw material for the preparation of anilin colors, but finds no industrial application for this purpose, because of the low price of coal tar and the fact that the composition of the latter is better known.

In addition to the tar separated by settling, the crude pyroligneous acid contains considerable tar held in solution by the acids and alcohol present, which is recovered when the crude acid is distilled, and constitutes what is known as "boiled tar." It may be sold as such or burned under the retort, or it may be mixed with the raw tar and subjected to any desired treatment.

Wood tar, which varies in character with the kind of wood from which it is obtained, is a thick, dark-colored, viscous material still containing some acetic and other acids, and has a specific gravity of about 1.05 to 1.15. It consists when derived from hardwood chiefly of paraffins, toluene, xylene, cresol, guaiacol, phenol, and methyl derivatives of pyrogallol. The tars derived from coniferous woods constitute the chief tars of commerce, and are particularly rich in terpenes, contain considerable quantities of rosin, and have a much greater commercial value than those derived from hardwoods. By far the greater part of the tar derived from hardwood distillation is burned under the retorts.

The general composition of various tars is shown in the following table:

General composition of various tars.

Kind of tar.	Specific gravity.	Acetic acid.	Light oils.	Heavy oils.	Pitch.	Gas and loss by distillation.
		Per ct.	*Per ct.*	*Per ct.*	*Per ct.*	*Per cent.*
"Meiler" tar from S. Austrian black fir	1.075	20	10	15	50	5
"Meiler" tar from Bohemian pine	1.116	10	5	15	65	5
Retort tar from Salzburg	1.180	10	10	15	55	10
Tar from distillation by superheated steam	.....	5	20	25	30	5
Tar from Douglas fir:						
Wood distilled below 700° C	1.000	.....	8	10	18	.....
Wood distilled below 420° C	1.075	.....	18	23	39	.....

The crude or raw tar may be handled in several ways. It may be burned under the retorts, sold as crude tar, or subjected to fractional distillation for the isolation of its several constituents. To effect this the tar is placed in a suitable still and heated. When mixtures of volatile liquids are heated sufficiently high the distillate does not, as a rule, have the composition of the mixture in the still, but the various constituents pass over in a more or less pure form between certain definite temperatures. This method of separating the product in the still into its various components is known as fractional distillation,

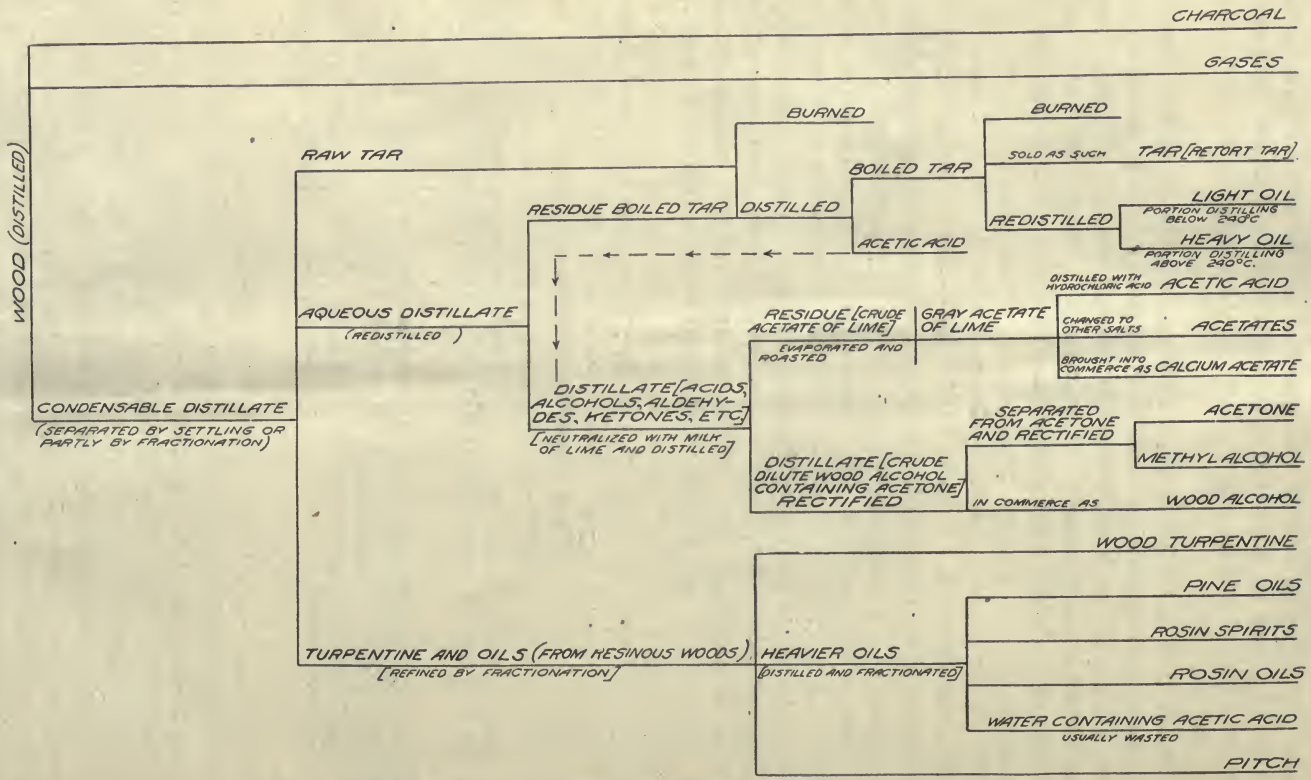


FIG. 14.—Diagram showing the processes and products of the destructive distillation of wood.

each portion as it distils or passes over being received separately from the other portions and called a fraction. Figure 14 shows graphically what products are derived from the destructive distillation of wood, and the subsequent separation of these products by fractional distillation. In the distillation of tar, iron stills are employed and the first fraction or portion obtained consists of acetic acid and alcohol mixed with some of the light oils. The light oils distil below 150° C. and have a specific gravity of from 0.966 to 1.000; the heavy oils distil above 150° C., have a specific gravity of from 1.014 to 1.021, and contain creosote, toluene, and paraffin bodies. The pitch, which constitutes from 50 to 65 per cent of the material, remains in the retort when the distillation is complete.

These several fractions, or portions, may be further purified, acetate of lime and alcohol being recovered from the first fraction, while the oily distillates are neutralized with milk of lime and redistilled. The light oils distilling below 150° C. are used as solvents and for varnish making, while those distilling at 150° to 250° C. are treated several times with alkali (boiling the alkaline solution in the air to oxidize impurities) and acid alternately and redistilled. The distillate obtained at from 200° to 250° C. is commercial wood creosote, which has a yellow or brownish color and a smoky aromatic persistent odor different from that of carbolic acid. This is agitated with strong soda, the aqueous layer drawn off is rejected, the remaining oil is mixed with sulphuric acid and allowed to stand until creosote oil separates, when this is driven off with steam and redistilled finally from glass retorts. The creosote obtained boils between 205° and 220° C. and has a specific gravity of from 1.030 to 1.080. It contains from 50 to 60 per cent of guaiacol ($C_7H_7O.OH$) and creosote ($C_8H_9O.OH$), and small quantities of other higher phenols. This product is a powerful antiseptic and is used as a disinfectant and preservative. The oils distilling above 250° C. are used for burning.

Stockholm tar and pine tar or pitch, made by distilling pitch pine or other coniferous woods in heaps covered with earth (see fig. 2), differ in composition from hard-wood and from pine-wood tar made in retorts and are regarded as more valuable. They are used for tarring ropes, calking ships, making soaps, for timber preservation, pitching barrels, and in preparing medicine.

Wood Oil.

When a crude aqueous distillate (see p. 32) is first distilled in order to separate acids, alcohol, and acetone from the tar, some of the lighter oils which are present distil with the acid and alcohol, and finally remain in the alcohol still, or, if distillation is carried further, they pass over in the last stages and separate as an oily layer. This

oil may be again distilled to recover any alcohol it contains, leaving the light wood oil, which is very inflammable and for which no profitable use other than burning has been devised.

Additional Oils Obtained From Resinous Woods.

Resinous woods are distinguished from hardwoods in yielding a much larger percentage of oils when distilled. Some of these oils exist naturally in the wood, while others are derived from the breaking up of natural resins. When wood is gradually heated as in destructive distillation, and the temperature in the retort rises above 100° C., these oils mixed with water begin to pass over or distil, and continue with rising temperature until the distillation of the wood is complete. The oil passing from the retort at any moment may be different from that which passed previously and from that which follows it, so that in practice the distillate is a mixture of compounds having closely related chemical and physical properties, and this mixture increases in density and the boiling point rises with the temperature in the retort. Below the temperature of 250° C. the oils are almost colorless, and there is but little if any breaking up of the natural resins, those that have distilled being naturally in the wood. When, however, the temperature in the retort rises above 200° C., the wood substance begins to char, giving to the products their characteristic smoky odor. Consequently, in order to obtain a turpentine free from this odor the temperature of the retort must not rise above 200° C. until the turpentine is completely distilled. At approximately 250° C. or above the lighter resins begin to break up, yielding oils which boil at from 97° to 250° C. When the temperature in the retort rises above 300° C. the heavy resins or rosin breaks up, yielding 3 to 7 per cent of light oils, known commercially as "rosin spirits" or "pinoline," boiling at from 97° to 250° C.; 75 to 85 per cent of heavy oils, boiling at from 250° to 450° C., known as "rosin oils," and water containing about 1 per cent of acetic acid. The oils distilling above 200° C. are contaminated by products derived from the breaking up of the wood substance, and these products mask especially the odor of the oils specified so that they do not have the characteristic rosin-oil odor. By proper methods of treatment and fractional distillation oils of different physical and chemical properties may be obtained, and a number of such oils are on the market under various trade names. Some of these oils have not yet found a regular sale, however, owing to the fact that their composition is not definitely known.

This product when properly made and refined has a specific gravity of from 0.860 to 0.880 at 20° C., though the first runnings from the still may have a lower and the last runnings a higher specific gravity; 95 per cent should distil between 150° and 185° C. This turpentine closely resembles spirits of turpentine from gum in most of its properties, and sells for from 2 to 10 cents less per gallon (depending on the care with which it has been refined) than gum spirits, for which it has been used as a substitute and adulterant. The processes of production and the technical value of this material are now being studied, but as the work is not completed no conclusion as to the relative value of wood turpentine as compared with gum spirits can be given at present.

A few words may be of interest, however, as to the best methods of producing, refining, and marketing this article. When wood turpentine was first placed upon the market it was very irregular in composition, owing to the fact that but little was known of its nature and producers were unacquainted with the proper methods of refining. As has been stated, turpentine as commercially produced is not a definite compound, but a mixture of closely related terpenes, and consequently it differs from moment to moment while distillation is taking place and its distilling temperature rises, so that the turpentine obtained at the close of a distillation is much heavier and differs in many ways, particularly in odor and color, from the first runnings from the still. This statement applies as well to gum spirits. The distiller seldom realizes the importance of this fact as affecting the uniformity of this product. In a few instances the gravity of the distillate is taken as the turpentine passes from the condensers, and if the hydrometer is carefully watched and the specific gravity is not allowed to rise above 0.875, the resulting turpentine is fairly uniform and satisfactory. As a rule, however, the close of the turpentine distillation is determined by the appearance of the oil, the formation of beads or foam on the surface indicating that heavier oils are beginning to distil. As this point is usually not carefully watched, the result is that the product of a plant differs from day to day in color, odor, and specific gravity, and its market value is lowered accordingly.

Although considerable improvement has been made, wood turpentine still varies greatly in composition, much to its detriment commercially. That produced by steam distillation has, in well-refined turpentines containing but a small amount of heavy oils, a pleasant, fresh pine odor and but little color, while the heavier portions of the steam-distilled oils have a more penetrating and lasting odor, somewhat resembling that of camphor, and the more of these heavy oils the turpentine contains the stronger its odor and the more it

differs from gum turpentine in all its properties. Turpentine produced by destructive distillation has a pungent, smoky odor, which the most careful refining will not entirely eliminate, and is usually more highly colored than the steam-distilled product.

The general character of the turpentine is determined largely, therefore, by the method of production, but it is further modified by the care with which it is refined. Every precaution should be taken to insure that the temperature does not rise sufficiently high to drive over the heavy oils. If the refining still is heated directly with fire, a thermometer may be placed in the liquid and the heat so regulated that its temperature does not rise above 220° C.; or, if the still is properly constructed, the product may be controlled by taking the specific gravity of the distilled and cooled turpentine with an accurate hydrometer.

If the crude turpentine is steam refined by passing a current of live steam through it, water and turpentine distil together at from 97° to 99° C., and after the lighter portions of the crude oils have distilled, heavier oils, which are always present in crude steam-distilled turpentine (owing to the fact that these oils distil below 100° C. when mixed with water), are also carried over, and these, in proportion to the quantity present, seriously affect the specific gravity, drying properties, and odor of the refined products. It is of the utmost importance, therefore, that toward the close of the distillation the specific gravity be carefully noted, using an accurate hydrometer, and when the gravity of the last portions distilling has risen to 0.875 the distillate should no longer be collected as turpentine.

By whatever method it is refined, the redistilled turpentine should be stored in a reservoir into which a large quantity is run, and from which it is barreled from time to time. With these precautions, the turpentine will be uniform in specific gravity, color, odor, flash point, and drying properties, and will agree closely in many of the physical tests with gum spirits, from which it will differ more or less in odor and color, according to the method of production.

PINE OILS.

In redistilling, below the temperature of 250° C. in the retort, the crude oils obtained in the distillation of resinous woods, there is no sharp distinction in properties or composition to be drawn between the oils obtained. Thus the oils that pass above 185° C. differ from the last fraction of turpentine but little; indeed, there is no clear-cut distinction in these oils until rosin begins to break up into rosin spirits and rosin oils. For convenience, therefore, all these oils distilling above turpentine (185°) and below the temperature at which rosin "breaks up" may be classified as pine oils, and they may be

further fractionated into a number of portions or fractions. These oils are suitable for use in making varnishes, soaps, disinfectants, paints, inks, etc.

When, in the distillation of resinous woods, the temperature rises above 250° C., not only is the wood attacked, but the resins in the wood also begin to break up, so that, with the acids, alcohols, ketones, oils, etc., formed from the wood, rosin spirits and rosin oils are formed from the rosin, and, if the latter are allowed to mix with the turpentine driven off at lower temperatures (which is always the case in straight destructive distillation), it is impossible to separate them perfectly from the turpentine in subsequent refining, because of the low boiling point of the rosin spirits. For this reason the odor of destructively distilled turpentine differs from gum spirits or steam-distilled wood turpentine and closely resembles that of rosin spirits.

ROSIN SPIRITS.

This product has a specific gravity ranging from 0.856 to 0.883 and a boiling point varying from 80° to 250° C. It has a peculiar odor, and, with the exception of wood turpentine, is the best substitute known for gum turpentine, being much used in the manufacture of the cheaper grades of varnish and as an illuminant. It contains as a characteristic constituent heptine (C_7H_{12}), which boils at 103° to 104° C., has a specific gravity of 0.8031 at 20° C., and absorbs oxygen readily.

ROSIN OILS.

Crude rosin oils have specific gravities varying from 0.960 to 1.0, while the refined oils vary from 0.960 to 0.990 and boil at from 300° to 400° C. They are largely used in the preparation of axle grease and other low-grade lubricants; also in the manufacture of printing inks, leather dressing, and cement, and as an adulterant for other oils.

TAR OILS.

The tar oils are obtained by distilling tar, and have many properties in common with rosin spirits and rosin oils. Those boiling at from 97° to 240° C. closely resemble rosin spirits, while those boiling above 240° C. contain phenol, creosote, rosin oils, etc., and, when freed from naphthalene and anthracene by cooling and from phenol and creosote by treating with alkali, are used as adulterants of lubricating oils.

AQUEOUS DISTILLATE OF CRUDE PYROLIGNEOUS ACID.

General Treatment for the Separation of Acetic Acid and Methyl Alcohol.

This distillate, comprising from 30 to 50 per cent of the weight of the wood, contains as its chief constituents, methyl alcohol (4 to 6 per cent), acetic acid (8 to 14 per cent), acetone (0.2 per cent), and tar held in solution by the acids and alcohol present, the balance being practically all water contained in the wood and resulting from its decomposition. The distillate is a dark red liquid having a strong acid reaction and an empyreumatic odor. Its specific gravity varies with the amount of water in the wood and the character of wood used, but usually falls between 1.020 and 1.050. This crude liquor is used to a limited extent in making "pyrolignite of iron," or "black iron liquor," an impure acetate of iron used in dyeing and calico printing. There are a number of different methods followed for separating the tar from this aqueous distillate and the several valuable constituents of the latter from each other. As has been said, raw tar is usually separated by settling all the liquors in large wooden vats, but even under the most favorable conditions the crude liquor still contains, dissolved in it, considerable quantities of tar, which interfere seriously with the purification of acetate of lime and alcohol prepared therefrom. In practice one of two general methods is used in handling the settled crude liquor:

(1) It is neutralized directly with lime and the alcohol distilled. The resulting calcium acetate is much contaminated with tar, and when evaporated and dried at about 125° C. forms the commercial "brown acetate of lime," containing from 65 to 75 per cent of real acetate of lime $(C_2H_3O_2)_2Ca$, the balance being tarry matter, calcium carbonate, and water.

(2) The crude pyroligneous acid without previous neutralization is distilled from the tar it contains. This is the better practice, and here again one of two procedures may be followed:

(*a*) Distil the alcohol, acid, and other volatile constituents, leaving only tar (boiled tar) in the still. Then carefully neutralize this distillate with milk of lime, force it to a still (lime-lee still, fig. 15) and redistil. Alcohol, aldehyde, and ketones pass over, while the acetic acid remains in the still in combination with lime. The most perfect separation and highest yields are obtained by this method.

(*b*) In the second procedure the alcohols, aldehydes, and ketones are separated from the acids by fractionation, using a column still (fig. 12). The first fractional portion, containing alcohol, acetone, and other compounds having low boiling points, but not the acids, is received in the alcohol vat until its density reaches 1.000. The second fraction or portion contains the acids and is received in the

acid vats, distillation being continued until only tar (boiled tar) remains in the retort.

In both cases the substance produced by treating the acid solution with milk of lime is known as "gray acetate of lime." The liquor containing the acetate, whether brown or gray, is pumped to copper evaporating pans (fig. 12, G_1–G_2), which are usually placed on the brickwork over the retort and the solution evaporated until the acetate begins to crystallize out, when it is transferred to a drying floor and stirred frequently until sufficiently dry. Gray acetate of lime contains from 80 to 85 per cent of actual acetate, the balance being tarry matters, calcium carbonate, and water. The gray acetate is used for the manufacture of acetic acid and other acetates and is largely employed in calico printing. It may be further purified by dissolving in water, filtering through boneblack, and evaporating the solution to 1.16 specific gravity, when the acetate crystallizes in small odorless needles which constitute the raw material from which acetone is made.

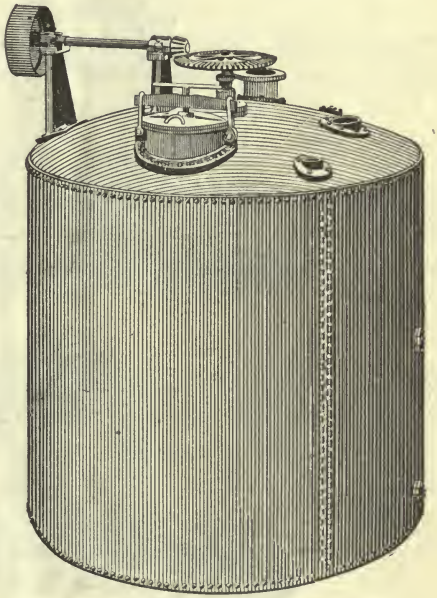


FIG. 15.—Liming still.

ACETIC ACID.

Commercial acetic acid is produced from gray acetate of lime, or from the brown acetate previously heated to about 230° C. to destroy tarry matter, by distilling with concentrated hydrochloric acid or with sulphuric acid (fig. 16). The latter is rarely used, as the calcium sulphate formed is difficult to remove from the stills and the impurities in the acetate reduce the sulphuric to sulphurous acid, which contaminates the acetic acid. A single distillation yields a slightly colored solution, containing 30 to 50 per cent of acid, which may be further purified by treating with potassium bichromate or permanganate and redistilling. The first portion of the distillate is contaminated with formic, proprionic, and butyric acids and with empyreumatic oils, but the subsequent portions are nearly free from impurities.

Glacial acetic acid is prepared by heating fused sodium acetate with concentrated sulphuric acid in a porcelain-lined or earthenware still and then distilling, when a nearly anhydrous product is obtained,

which crystallizes if cooled to 16.5° C. It has a specific gravity of 1.0553 at 15° C. and boils at 119° C.

The ordinary acetic acid of commerce contains about 30 per cent of anhydrous acid, has a specific gravity of about 1.040, and is slightly colored. It is used in the preparation of acetates, the manu-

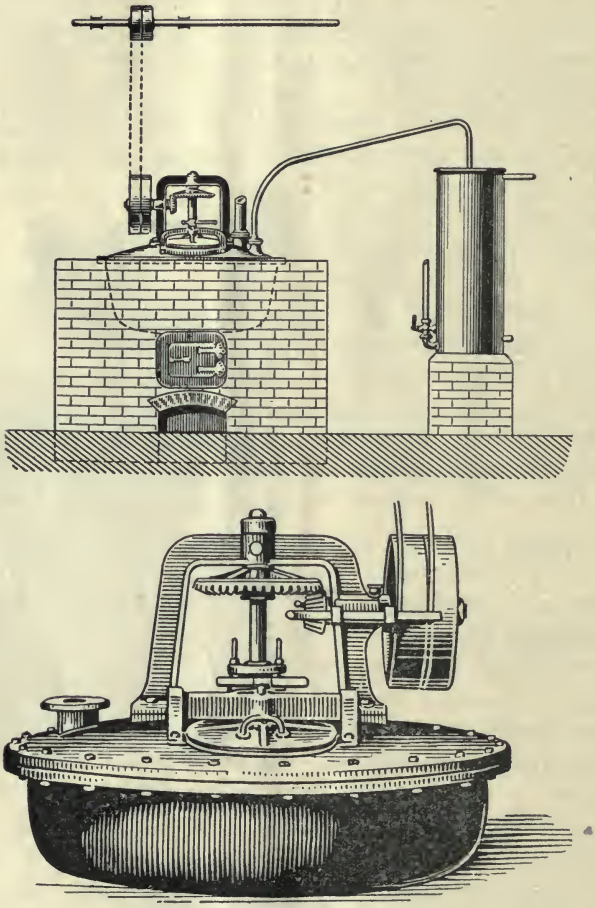


FIG. 16.—Still for preparing acetic acid from acetate of lime, with detail of acetate pan.

facture of white lead, and in pharmacy. Some pure acetic acid made from wood by distillation is used as vinegar, but such preparations have not the characteristics of fruit vinegar.

In addition to acetate of lime and soda already described (p. 32), the following acetates are prepared for industrial purposes:

ALUMINUM ACETATE.

This product is made by dissolving aluminum hydroxid in an excess of acetic acid, or by decomposing lead or calcium acetate with aluminum sulphate. It is known as "red liquor" and is largely used in dyeing and calico printing. Red liquor made from calcium acetate is to be preferred.

CHROMIUM ACETATE.

This chemical is made by dissolving chromic hydroxid in acetic acid, or by treating chromic sulphate solution with calcium or lead acetate. It is used as a mordant in calico printing.

COPPER ACETATE.

Copper acetate may be obtained by dissolving verdigris (copper carbonate) or copper oxid in acetic acid, but the best is made by decomposing a copper-sulphate solution with lead acetate.

LEAD ACETATE.

Lead acetate, or sugar of lead, is prepared by dissolving litharge, or red lead, in acetic acid, and is used for making other mordants and for manufacturing chrome yellow. When excess of litharge is employed, basic acetates are produced.

SODIUM ACETATE.

Sodium acetate is prepared by neutralizing dilute acetic acid with sodium hydroxid or sodium carbonate and concentrating the solution. When the sodium acetate crystallizes out, it may be purified by recrystallization or by fusion. It is chiefly used in making pure concentrated acetic acid, certain diazo bodies, and as a developer for azo dyes in which the color is made on the fiber.

CRUDE METHYL ALCOHOL AND ACETONE.

The distillate obtained from the acetic acid or calcium acetate (p. 32) in the lime-lee stills contains the following: From 8 to 10 per cent of methyl alcohol, acetone (methyl acetate, and some acetic acid if the process has not been carefully conducted), aldehydes, allyl alcohol, dimethyl acetone, methylamine, ammonium acetate, small quantities of ammonia and amines, oily hydrocarbons, and ketones. These latter oily hydrocarbons and ketones render the whole turbid when the alcohol is diluted with water. It is necessary, therefore, to remove these impurities, which may be done by careful fractionation of the methyl alcohol in a column still (fig. 12, H_1, H_2, H_3), the last runnings from which contain the oily impurities, which become milky when diluted with water, and should not be allowed to mix with the alcohol, but may be further treated by again fractionating

the last runnings from a number of distillations for the recovery of the methyl alcohol which they contain. Or these impurities may be removed from the weak alcohol by diluting with water to a specific gravity of about 0.935, or until it is turbid from the precipitation of the oils and ketones; allow it to stand until these rise to the top as a distinct oily layer and remove by skimming. The alcohol may then be again distilled in a column still. The product in either case is crude methyl alcohol, or "wood spirit," of a slightly yellow color and a specific gravity of about 0.827. This product contains approximately 80 per cent of alcohol, 6 per cent of acetone, and 12 per cent of water, besides traces of empyreumatic products that give it a disagreeable taste and smell. The crude article is largely used for the preparation of formaldehyde, as a solvent in lac and varnish making (for which purpose the presence of acetone is rather advantageous), and also for denaturing ethyl or grain alcohol for industrial uses. By again distilling over lime all but about 3 per cent of water may be removed from the crude alcohol, which still contains acetone, etc.

The compositions and properties of some wood alcohols are given in the following table prepared by Klar:[a]

Composition of wood alcohols (Klar).

Kind of wood alcohol.	Color.	Miscibility with water.	Tralles.	Acetone.	Spirits required to decolorize 100 cc of potassium bromid and bromate solution.
			Degrees.	*Per cent.*	*cc*
Crude spirit from silesia	Yellow	Very turbid	80	6.44	50.00
Crude spirit	do	Turbid	80	10.00	15.90
Rectified spirit	White	Clear	94	5.60	79.30
Rectified spirit from the Hartz	do	do	92 to 95	37.46	14.5
Crude spirit from the Hartz	Yellow	do	85	20.94	51.20
Crude spirit, American	Yellow-brown	do	80	11.00	65.00
Rectified wood spirits, "A" xylolyse	Almost white	do	98 to 99	4.80	52.00
Rectified wood spirits, "B" xylolyse	Yellowish	do	95	13.72	19.40
Rectified wood spirits, Westphalian	White		93 to 94	4.50	70.00

The specifications adopted by the Treasury Department for methyl alcohol for denaturing grain alcohol are summarized as follows:

The methyl alcohol submitted must be partially purified wood alcohol, obtained by the destructive distillation of wood. It must conform to the following analytical requirements:

Color.—This shall not be darker than that produced by a freshly prepared solution of 2 cc of tenth-normal iodin diluted to 1,000 cc with distilled water.

Specific gravity.—It must have a specific gravity of not more than 0.830 at 60° F. (15.56° C.) corresponding to 91° of the Tralles scale.

[a] J. Soc. Chem. Ind., 1897, 16; 724.

Boiling point.—One hundred cubic centimeters slowly heated in a flask under prescribed conditions must give a distillate of not less than 90 cc at a temperature not exceeding 75° C. at the normal pressure of the barometer (760 mm).

Miscibility with water.—It must give a clear or only slightly opalescent solution when mixed with twice its volume of water.

Acetone content.—It must contain not more than 25 nor less than 15 grams per 100 cc of acetone and other substances estimated as acetone when tested by the method of Messinger.

Esters.—It should contain not more than 5 grams of esters per 100 cc of spirit, calculated as methyl acetate.

Bromin absorption.—It must contain a sufficient quantity of impurities derived from the wood, so that not more than 25 cc nor less than 15 cc shall be required to decolorize a standard solution containing 0.5 gram of bromin.

In addition to the above requirements, the methyl alcohol must be of such a character as to render the ethyl alcohol with which it is mixed unfit for use as a beverage.

PURE METHYL ALCOHOL.

As acetone and methyl alcohol form mixtures having a minimum boiling point, it is impracticable to separate them by simple distillation, and therefore other means are employed. The alcohol is treated with chlorin, which, combining with the acetone, forms chloracetones having high boiling points and from which the alcohol may be separated by distillation. Another method is to add iodin and caustic soda, which form a precipitate of iodoform with acetone, which may be removed by filtration or sedimentation, the alcohol being subsequently distilled.

Still another method, and the one probably most generally used, is to treat the alcohol with calcium chlorid, with which alcohol combines forming a compound having the formula $CaCl_2.4CH_3OH$, stable at 100° C. This compound is heated gently until the acetone is driven off, treated with hot water under pressure, and the methyl alcohol distilled. This distillate is again rectified and redistilled over lime until it contains from 95 to 99 per cent of alcohol. This product is known to the trade as "Columbian Spirits," "Louis d'Or," "Eagle Spirits," "Colonial Spirits," or refined wood alcohol, which has a spirituous odor, a specific gravity of 0.8142, and boils at 66° to 67° C. at 0° It is miscible in all proportions with water, ordinary alcohol, and ether, and is an excellent solvent for fats, oils, and resins. It is extensively used in the manufacture of anilin colors and smokeless powder, in the making of hats, etc.

ACETONE.

Pure acetone is a colorless liquid having a peculiar ethereal odor and a burning taste, a specific gravity of 0.814, and a boiling point of 56.3° C. at 0°. It is miscible with ether, alcohol, and water in all proportions. Commercial acetone should not have a specific gravity greater than 0.802 at 15° C., and four-fifths of it should distil below

58.8° C. It is an excellent solvent for resins, gums, camphor, fats, and gun cotton, and is largely used in the manufacture of smokeless powder, the preparation of celluloid goods, chloroform, iodoform, and sulphonal.

In addition to that produced directly in the distillation of wood and separated from methyl alcohol as above described, large quantities are made from gray acetate of lime by dry distillation at high temperature, decomposition taking place according to the following formula: $(C_2H_3O_2)_2Ca = CaCO_3 + CH_3.CO.CH_3$. The distillation and decomposition is conducted in an iron retort, with constant stirring. The distillation takes place in three stages: At first water containing a small percentage of acetone comes over; in the second stage, when the temperature of the mass has risen to 400° C., acetone oils are obtained. The dark brown, highly inflammable distillate separates into two layers on standing, the top layer consisting of the so-called "heavy acetone oils" and the lower of acetone and light acetone oils dissolved in water. The following table gives the percentage yield of products obtained by the distillation of gray acetate of lime:

Products obtained by distillation of gray acetate of lime.

Products.	Amount present.	Specific gravity.	Actual acetone.
	Per cent.		*Per cent.*
Acetone water	7 to 15	1.010	3.0
Crude acetone	32	.900	67.5
Total distillate	42	.930	53.5

The yield of acetone is about 20 per cent of the calcium acetate, or about 13 per cent when made from 40 per cent acetic acid.

In preparing pure acetone the crude distillate obtained, which contains higher ketones, aldehydes, etc., is treated with milk of lime and allowed to stand for some time. The supernatant oily layer is diluted with water and distilled in a column still, yielding as a main fraction a nearly pure product (99° to 99.5° Tralles), which does not become turbid when mixed with water. Another distillation removes traces of aldehydes and empyreumatic materials. The first and last fractions obtained in the above distillation, together with oils recovered from the clarification with milk of lime, are mixed and redistilled, yielding another portion of commercial acetone. The residual oils are the so-called acetone oils of commerce, known as light oils, boiling between 75° and 130° C., and heavy oils boiling between 130° and 250° C. They may be used as denaturing agents, as a means for purifying raw anthracene and in secret manufacturing processes.

RECOVERY OF CERTAIN WOOD PRODUCTS BY TREATMENT WITH CHEMICALS.

In addition to the distillation methods already mentioned resinous woods may be treated by other processes for the recovery of the turpentine and rosin which they contain. For various reasons these processes have received but little attention in the past. Their successful operation requires more chemical and technical knowledge, and a more extensive plant than the methods commonly employed in recovering turpentine and rosin. Heretofore the value of the products, some of which were not utilized, did not justify the greater cost of these processes. However, as a good grade of light wood contains from 15 to 30 per cent of rosin and turpentine which may be recovered by chemical treatment, and as the extracted wood is suitable for paper making, present prices justify a brief consideration of these processes.

TREATMENT WITH SODA, SODA ASH, OR VOLATILE SOLVENTS.

When woods are treated with boiling alkali solutions, with or without pressure, turpentine is volatilized, and rosin is dissolved together with other noncellulose matter. The turpentine distils off and the dissolved matter may be subsequently washed out and recovered as a soap, in which form it may be used as sizing material for paper and in making soap, or the alkali resinate may be thrown out of solution by neutralization and recovered as an impure rosin. In either case the rosin or resinate may be destructively distilled, if desired, for the preparation of rosin spirits and rosin oils. By burning the residue in the retort in a current of air, black ash, an impure alkali carbonate, is recovered, which may be used again for the extraction of turpentine and rosin. Rosin and turpentine may be recovered in the manufacture of paper pulp from pine wood by this treatment.

It has been proposed to recover turpentine and rosin by extracting the finely chipped wood with a volatile solvent, such as benzine, alcohol, etc. In this case the rosin and turpentine obtained are of exceptional purity, but the practicability of recovering the solvent economically remains to be demonstrated. This process also involves considerable risk from fire.

Both processes are particularly suited to the treatment of sawdust and other finely prepared waste wood, which are destructively distilled only with great difficulty. Both of these methods for the recovery of turpentine and rosin are now being investigated in this laboratory for the purpose of determining their value as industrial processes. As far as is known turpentine and rosin are not recovered with volatile solvents in actual practice.

PREPARATION OF ETHYL ALCOHOL FROM SAWDUST.

Another product which may be prepared by the chemical treatment of wood, preferably sawdust, is ethyl alcohol, which is made by treating the wood with sulphurous acid, thus partly converting it into fermentable sugar, neutralizing, and fermenting with yeasts.

The alcohol produced is very similar to that produced by hydrolizing starch with acids and is in every way suitable for industrial purposes. A yield of 25 gallons of industrial alcohol per long ton of sawdust is claimed for this process.

Numerous attempts have been made to obtain sugar or alcohol from wood by treating it with hydrochloric or sulphuric acid, but the yields have not been large enough to make the process commercially successful.

PRODUCTION OF ACETIC ACID AND ACETATES BY FUSION WITH ALKALIES.

As the market for methyl alcohol may be seriously affected, at least temporarily, by the use of tax-free denatured ethyl alcohol in those industries heretofore using methyl alcohol, any method for increasing the yields of the other products of distillation is not without interest at this time. In addition to the ordinary destructive distillation process, acetic acid may be obtained from wood by submitting it to alkaline or acid hydrolysis, or by oxidizing with acids or alkalies. The hydrolytic process and oxidation with sulphuric acid do not give larger, if as large yields, as destructive distillation. Oxidation with dilute nitric acid yields from 10 to 18 per cent of acid, while the maximum yields are obtained by treating with the alkaline hydrates at 200° to 300° C., the yield being from 30 to 40 per cent of the weight of the wood together with a considerable quantity of oxalic acid. The chief factors governing the yield are the ratio of alkalies to sawdust, the kind of alkali used, the time of heating, and atmospheric oxidation. The highest yields are obtained when three parts of potassium hydrate are used to one part of sawdust and the mixture is heated for a long time with or without exposure to air.

The procedure is almost identical with that used in the manufacture of oxalic acid; and, as would be expected, oxalic acid is also obtained in considerable quantity, depending on the temperature at which the operation is conducted. No application of this process in this country is known to the writer, although it is patented and used in the production of acetates from soda-pulp liquors both in England and Germany.

MANUFACTURE OF OXALIC ACID.

The manufacture of oxalic acid is apparently an entirely neglected industry in this country and is one which should receive consideration from chemical manufacturers, and could undoubtedly be made an industry of considerable value. As will be seen from the following table imports are steadily increasing and have reached quite a large figure:

Quantity of oxalic acid imported, 1891–1905.

Year.	Amount.	Value.
	Pounds.	*Dollars.*
1891	2,743,222	200,595
1895	2,889,513	189,506
1899	3,981,768	246,027
1900	4,990,123	275,747
1904–5	7,906,886	360,951

While from the point of view of the utilization of mill wastes this industry must be of minor importance for some time, there seems to be an opening for several plants of sufficient capacity to supply our home demand, and probably an export trade in oxalic acid could be developed, just as has been done in the case of acetate of lime. The rapid growth of imports during the past four years promises well for the future of this industry in the United States.

Oxalic acid is prepared from sawdust by fusing with caustic alkalies. To prepare the caustic alkali solution, potassium and sodium carbonates are mixed in such proportion that after causticizing (treating with lime water, whereby sodium and potassium hydrates are produced and calcium carbonate is precipitated) the proportion of potassium hydroxid to sodium hydroxid shall be about 4 to 6. A mixture of the two salts is dissolved in about 8 times its weight of water and made caustic by boiling in an iron pan with slaked lime. After the carbonate of lime has settled, the lye is drawn off into another pan and concentrated to about 1.3 to 1.4 specific gravity. Sawdust, free from large pieces of wood, is now mixed with the lye in such quantity that there shall be two parts by weight of alkali to one part of sawdust. The whole is thoroughly mixed, after which all the liquid should be taken up by the sawdust. The mass is then spread out to a depth of from one-half to three-fourths inch on heating plates of iron about 6 feet in diameter, with a 2-inch rim. It is stirred continuously during the conversion to oxalate. The temperature should be raised gradually, but care should be taken that it does not exceed 240° C., as oxalic acid is destroyed by higher temperatures. To prevent too high heating it is best to heat the plates with hot gases rather than by direct fire, as by the aid of dampers the temperature

of the plates can be quite readily controlled. In the first part of the process the mass loses water and turns darker until it becomes a deep brown and evolves a peculiar odor. When the temperature reaches about 180° C., the mass begins to lose color again and becomes a greenish yellow. The temperature is then gradually raised to 240° C., at which point it is held until the mass no longer contains particles of wood and is of a greenish white color, the total time required being about six hours. The mass is then removed from the plates and cooled or immediately dissolved in hot water and the liquid concentrated to about 38° B., when it is run into small crystallizing pans in which, on rapid cooling, nearly all of the sodium oxalate separates, leaving potassium carbonate, caustic soda, caustic potash, humus compounds, and a little oxalate in solution. The sodium oxalate may be freed from the mother liquor by draining and washing or by centrifuging.

The mother liquors are evaporated to dryness, roasted in air, and causticized as before for use again. The sodium oxalate is dissolved in a very little boiling water, and sufficient thin milk of lime is run in, with constant stirring, to change all of the sodium oxalate to calcium oxalate and caustic soda. The mixture is run into settling tanks, where the oxalate of lime settles out and the supernatant caustic soda is run off and concentrated with the first wash water from the oxalate, mixed with caustic potash, and used for treating another lot of sawdust. After washing, the oxalate of lime is run into a lead-lined tank, stirred to a paste with water, and treated with dilute sulphuric acid of from 15° to 20° B., in such quantity that the mixture contains two equivalents of sulphuric acid to one of lime. The whole mixture is kept hot until a test shows no calcium oxalate present, when the calcium sulphate is allowed to settle, the clear solution containing the oxalic acid is drawn off, and the calcium sulphate washed with water. The first washings are added to the oxalic acid solution and the remainder is used to mix with the oxalate of lime in a subsequent decomposition. The calcium sulphate, or gypsum, thus produced may be disposed of as a fertilizer or, as it is very pure, may be used as a filler in paper making, or dehydrated and used as plaster of Paris. The solution of oxalic acid is concentrated in shallow lead pans until it is, in summer, 15° B., and in winter 10° B. It is then cooled to ordinary temperature, when the dissolved gypsum separates in crystals. The liquid is further concentrated to 30° B. and crystallized in shallow lead pans. These crystals are washed in a minimum quantity of cold water to remove adhering mother liquor, dissolved in boiling water, and cooled rapidly, when small crystals form. The product is commercial oxalic acid, and contains small quantities of sulphuric acid and oxalate of soda or

potash, from which it can only be freed by recrystallization in from 10 to 15 per cent hydrochloric acid. The mother liquors, from which nearly all of the oxalic acid has been separated, contain the excess of sulphuric acid used in setting oxalic acid free and some oxalic acid, and are used, after being brought to the desired strength by the addition of concentrated acid, for the decomposition of the next lot of oxalate of lime.

Light woods, such as pine, fir, and poplar, give the best yields, amounting to about 90 per cent of the weight of the dry wood, while the heavy woods—oak, beech, etc.—yield about 80 per cent.

Oxalic acid is largely used as a discharge in calico printing and dyeing, for bleaching flax and straw, for bleaching leather, and in the manufacture of formic acid.

SUGGESTIONS FOR THE DEVELOPMENT OF THESE INDUSTRIES.

The industrial processes briefly described in the preceding pages separate or prepare from wood certain chemical compounds, some of which are important articles of commerce, their total value per unit of wood being greater than that of the wood from which they are obtained. Thus, taking average yields of well-operated plants and valuing the products at current wholesale prices, a cord of wood may be said to yield the following approximate gross values:

Hard wood, destructively distilled	$11.00
Pine (good light wood)	25.00
Pine (good, steam-distilled)	7.00
Pine extracted with soda, soda pulp made	44.00
Pine extracted with volatile solvents and pulp made from residue	46.00
Pine extracted with volatile solvents and residue destructively distilled	26.00

No figures are given for oxalic acid, for the reason that the industry is undeveloped in this country, and while the gross values are much greater than those given in the preceding statement for other chemical products the cost of production is relatively much higher, and a theoretical statement in regard to its production might be misleading.

It must be fully understood that these values are given merely for purposes of illustration and are only approximate gross values, as the yield at any one plant may vary widely above or below those given. They are based on the yields from well-equipped and carefully operated plants using good grades of wood. The several products are priced as follows: Charcoal, 4 cents per bushel; 80 per cent alcohol, 30 cents per gallon; turpentine, 60 cents per gallon; rosin, $4 per barrel; tar, $6 per barrel; gray acetate, $2.50 per 100 pounds; unbleached soda pulp, 2 cents per pound.

From the gross values certain fixed charges must be deducted. They are cost of raw material at the plant; cost of operating (labor,

management, fuel); cost of containers for shipping products; insurance, depreciation, and repairs; interest on capital, etc.

It is beside the purpose of this circular to give an estimate of these gross values and fixed charges, and they are only mentioned here in order to point out briefly and in general terms some of the ways in which an inspection of numerous plants and laboratory work indicates that the net proceeds of several of the industries may be increased. Attention will be confined to a consideration of (1) yields, (2) operating expenses, (3) raw materials. As a matter of fact, however, these three headings are so intimately associated that the effect of any one of them on profits can not be entirely differentiated from that of the others.

YIELDS.

In the destructive distillation of wood the yields obtained in practice are much below those given under laboratory conditions. This may be due to destruction caused by local overheating in the retorts, loss of vapors around the doors of the retorts, incomplete carbonization, or imperfect condensation. Losses may also occur from incomplete or excessive overneutralization of acids with milk of lime, or to incomplete separation of alcohol and acids from the tar, or of alcohol from water. All of these points should receive the constant watchful attention of the superintendent, that such losses may be reduced to a minimum. Indeed, yields are largely controlled by the experience and technical knowledge of the superintendent. The almost total absence of chemical control in these industries doubtless accounts for many unprofitable plants, the source of whose failure can not be otherwise discovered.

OPERATING EXPENSES.

Inspection of destructive distillation plants leads to the conclusion that the expense of operating is largely increased by the employment of hand labor where machinery could often be used to better advantage. Thus, wood received is often handled several times before it is placed in the retorts. Nearly all round retorts are filled and emptied by hand. Storage room should be so arranged as to avoid handling the wood more than once after it is received. This is possible only when oven retorts are used, in which case the wood is not handled except when loaded on the retort cars, which are moved by power and emptied directly into railroad cars or storage bins, from which the charcoal may be taken automatically.

Great loss of heat and waste of fuel is occasioned by the practice of condensing and cooling to ordinary temperature the aqueous distillate (p. 32) and allowing it to stand for the purpose of settling out the tar.

Such methods appear illogical and unscientific, as the uncondensed vapors leaving the retorts contain sufficient heat to separate them into their three chief constituents—tar, acetate liquor, and dilute alcohol. The process may be greatly simplified in this way, as is shown in the following comparative statement of present methods and the suggested method. The present process involves the following independent successive steps:

(1) Cooling and condensing the tar, acids, alcohols, etc.
(2) Storing, settling, and separating tar from aqueous distillate.
(3) Redistilling tar from (2); cooling, condensing, and storing aqueous distillate, and storing tar.
(4) Redistilling aqueous distillate from (2); cooling, condensing, and storing distillate, and storing tar.
(5) Neutralizing, distilling, cooling, condensing, and storing distillate from (3) and (4).
(6) Fractionating distillate from (5).
(7) Evaporating, drying, and roasting residue from (5).

The operations under 3, 4, 5, 6, and 7 require a great amount of heat, which is entirely lost in 1, and which is obtained for these operations from additional fuel. The operations under 2, 3, 4, and 5 require apparatus and storage room, part of which is not needed with the modified system.

Under the modified system the heat lost at (1) in the present system is utilized to separate the constituents of the distillate without expense for fuel. Thus—

(1) Receive the tar, alcohol, and acid distillate in a closed still, from which the acid and alcohol will be distilled by their own heat.
(2) Pass the uncondensed vapors through milk of lime; the acids will combine with the lime and remain in the mixing vat while the alcohol distils by its own heat.
(3) Pass the uncondensed vapors of alcohol-water from (2) to a column still, and rectify as usual.
(4) Evaporate, dry, and roast residue from (2), as usual.

Such a procedure as this is perfectly feasible, can be made continuous, and will result in the saving of fuel, boiler capacity, apparatus, and storage room. Further, it will prevent any losses now due to incomplete condensation of vapors, which certainly occur at several points in the present system. The process can also be made largely automatic, resulting in more regular production, reduction of operating expenses, and in general economy and efficiency of the plant. Where resinous woods are distilled the distillate from the tar must be condensed in order to separate the turpentine and pine oils from the alcohol and acids.

The annual waste (in lumber sawmills), which is now sold for fuel in the United States, is, according to the Forest Service, equivalent to approximately 4,000,000 cords of wood, or within 800,000 cords of the amount now used in the destructive distillation (1,145,000 cords) and paper-making (3,647,000 cords) industries. If to this be added the waste, such as tops, lap, and dead and down timber left in the woods, this quantity is more than doubled, although no definite figures as to the total quantity can be given. The mill and forest wastes from resinous woods would yield a large portion of the turpentine and rosin now produced and several times as much soda pulp as is now made. The waste from the hardwood lumber industry would yield more charcoal, wood alcohol, and acetate of lime than is now being produced. The sawdust from the Southern pine mills alone will yield more oxalic acid than is now used in this country. The spruce and hemlock waste will yield at least one-half of the sulphite pulp now produced. The question is, Can these industries be most profitably conducted in conjunction with the lumber industry, or independently? While, perhaps, a categorical answer applicable to all conditions can not be given at present to this question the above-mentioned facts strongly indicate that the proper industrial location of the chemical industries using wood as a raw material is in conjunction or close affiliation with the lumber industry. Such combination means cheap raw material and fuel for these industries and increased profits for the lumber industry, as well as the removal of waste which otherwise seriously interferes with the use of the land and is a constant menace from fire.

It is seen that the gross values obtained per cord of wood are lowest when the wood is subjected to steam or destructive distillation, and it seems advisable, therefore, that attention be directed more to those methods of utilization which give larger gross values. Thus the recovery of turpentine and rosin by extracting with soda or volatile solvents, and using the residue for paper pulp or for making oxalic acid, are promising methods of utilizing pine wood that are receiving some attention from paper makers and investors, and their industrial value should be carefully determined. The demand for oxalic acid is, however, small as compared with available raw material, and could be readily supplied by a few well-equipped plants. In general, it may be said that all suitable wood should be used in producing the articles of greatest value, such as paper pulp, turpentine, and rosin, leaving oxalic acid to be obtained from part of the sawdust and destructively distilling only that wood which can not be more profitably utilized.

RETURN TO → MAIN CIRCULATION

ALL BOOKS ARE SUBJECT TO RECALL
RENEW BOOKS BY CALLING **642-3405**

DUE AS STAMPED BELOW

FEB 01 1996		
RECEIVED		
NOV 0 2 1995		
CIRCULATION DEPT.		

UNIVERSITY OF CALIFORNIA, BERKELEY
BERKELEY, CA 94720

FORM NO. DD6

U. C. BERKELEY LIBRARIES
C051402917

UNIV... CALIFORNIA ...

14 DAY USE
RETURN TO DESK FROM WHICH BORROWED
LOAN DEPT.
This book is due on the last date stamped below, or on the date to which renewed.
Renewed books are subject to immediate recall.

JUL 14 1966 4 1
JUL 14 '66 4 1 RCD
JUN 1 6 1974 1 4
REC'D CIRC DEPT JUN 11'74 X
AUG 29 1975
REC. CIR. AUG 29 '75
MAY 28 1981
REC. CIR. APR 28 1981
DEC 4 1983 --
REC. CIR. NOV 8 '83

LD 21A-60m-10,'65
(F7763s10)476B
General Library
University of California
Berkeley

YC 69407